VIBRATIONAL ANALYSIS AND THE SYMMETRY OF THE BENZENE MOLECULE

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DISSERTATION

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Deitz and Andrews (6) in 1932 made the first attempt to decide a question of molecular structure by a thermal-spectroscopic determination of symmetry number. In spite of the handicap of incomplete data and of a vibrational analysis made with the roughest sort of approximations, their effort produced the very reasonable value of six for the symmetry number, σ, of benzene. Definition of the symmetry number and the method of combining thermal and molecular information for the computation of σ are presented in detail in the paper of Deitz and Andrews.

Since 1932, much theoretical and experimental work has been carried out with the object of clearing up the problem of the internal frequencies of benzene. In addition, deficiencies in accuracy of the low temperature thermal data have lately been removed by Ahlberg, Blanchard, and Lundberg (1). Accordingly it is now possible to make a much more reliable calculation of σ for benzene.

The symmetry number of the particular type of molecule present in a gaseous system enters the expression furnished by statistical mechanics for the entropy, S_g, of that system. If all the components of this expression except σ can be evaluated, we can determine σ by an experimental evaluation of the entropy of the gas. The calculation of S_g requires a considerable amount of molecular information, namely the molecular weight, the moments of inertia, the complete set of vibrational frequencies, and the symmetry number. Granted a knowledge of all these items except σ, and given experimental access to S_g, σ becomes easily determinable. The moments of inertia can be computed without difficulty when geometrical data are available for the molecule. The essentially important item is therefore the complete set of vibrational frequencies, and the determination of this set by analysis of spectroscopic data on benzene is our chief problem.

The experimental data available for a determination of the thermal value of S_g are quite satisfactory. A survey of the estimated reliabilities of these thermal data leads to the conclusion that, barring the possibility of undiscovered transitions and of anomalous behavior of the heat capacity below 2°K., the thermal entropy of gaseous benzene at the boiling point is in error by about 0.5 per cent.

THE VIBRATIONAL FREQUENCIES OF BENZENE

The frequencies of the benzene molecule have been the object of much widely varied study, particularly since the discovery of deuterium. The number of investigators of this compound in the different fields of molecular spectroscopy has been quite large. The spectroscopic data have been summarized quite thoroughly by Ingold et al. (9). The values of Raman and infra-red frequencies which we have utilized are in essential agreement with those in the summaries. In addition the fact that benzene possesses particularly high symmetry has incited several theoretical attacks (3, 19, 21, 22) on the vibrational forms of the molecule. The most complete theoretical study is that of Wilson (21). In this paper Wilson not only obtained normal coördinates for the vibrations of benzene, but in addition suggested a simple and plausible potential system on the basis of which the equations for actual frequencies were worked out. These equations are quite helpful in interpreting observed frequencies, and are especially valuable for estimation of those frequencies which are not observable.

The benzene molecule possesses thirty degrees of vibrational freedom, of which ten are non-degenerate and ten doubly degenerate. The twenty distinct frequencies have modes of vibration which are predetermined by the symmetry of the molecule. The actual modes have been given by a number of investigators (9-VIII, 11, 20, 21). Of the twenty frequencies, four are obtained from the roots of a quartic equation, three from a cubic, five pairs from the roots of five quadratics, and three from the single roots of three linear equations. Wilson's article gives the explicit equations for all frequencies save those coming from the quartic and cubic. These latter he leaves in the form of secular determinants. The determinants have been expanded by Kohlrausch (11), whose expansion we have been able to check except for one considerable discrepancy: the first term in the coefficient of λ in the cubic as given by Kohlrausch is twice too large.

The evaluation of five of the six force constants of the Wilson potential scheme has been carried out by Kohlrausch for benzene and benzene-d_6. K and q (see table 1) may be obtained directly from frequencies ν_1 and ν_2 (Wilson's notation) and h from ν_{10}. k and H require more complicated determination, since the observable frequencies involving them derive from the quartic and cubic equations. Kohlrausch has evaluated k by assigning to the unobservable frequency ν_{12} a definite value of 1000 cm^{-1}.

We agree with this assignment and will list the arguments in its favor later on.

Kohlrausch used a graphical method for obtaining H from the quartic. His method seemed rather dubious to us, and we therefore devised several approximation methods of solving the four relationships between the force constants and the frequencies of the quartic. The approximation methods yielded values of q and k in good agreement with those found in other ways. The constant K, however, turned out to be somewhat lower than its value as found from ν_1 and ν_2, and H appeared to be rather too high. It is probable that the quartic is an equation of restricted validity, because of the overly simplified form of the potential function. H was therefore evaluated from the cubic, the frequencies of which are observable in the infra-red. The values of H we obtained from benzene and benzene-d_6, respectively, are in good agreement. On the other hand, Kohlrausch reports an increase of some 15 per cent in H for benzene-d_6 over that for benzene. This apparent increase is doubtless due to his interpretation of the infra-red band at 1440 cm.$^{-1}$ in benzene-d_6 as a fundamental, which interpretation may have been expedited by the previously mentioned error in the λ-term of the cubic. If this fundamental is identified with the 1330 cm.$^{-1}$ band, the value of H for benzene-d_6 lies within about 2 per cent of that for benzene. This assignment is supported by the calculated ratio for the benzene–benzene-d^6 shift, which can be determined with the help of Teller's unpublished theorem concerning isotopic vibrational shifts (see reference 9-VIII).

There are eleven frequencies in benzene which are observable in the Raman effect or in infra-red absorption. These eleven frequencies, constituting *nineteen* of the thirty vibrational degrees of freedom, are listed in table 1, with the corresponding calculated values. The only notable departure of calculated from observed frequency occurs in ν_{11}, where the discrepancy is as large as 15 per cent. The disagreement is puzzling, for there seems to be no explanation for the failure of the Wilson potential scheme for this particular mode of vibration. The failure of the assumed potential system under such apparently favorable circumstances indicates that one must not be too sanguine about the calculation of unobserved frequencies.

The remaining eleven degrees of freedom are represented by nine unobservable frequencies. These nine frequencies may be divided into the five non-degenerate vibrations which take place in the plane of the ring, and the four vibrations, two of which are degenerate, that do not preserve the plane of the ring as an element of symmetry.

The force constants involved in the five planar vibrations, namely K, q, k, and H, can be determined from the observable frequencies. Accordingly the calculation of these unobservable frequencies by means of Wilson's

equations is possible. We have made such a calculation using the values of K, q, and k listed in table 1. In addition we felt that it would be worthwhile to attempt to improve the value of the constant H by taking into account repulsion between adjacent hydrogen atoms. H can be considered as made up from several components, namely the "directed" C—H valence bond, repulsion between the hydrogen atom and the two carbon atoms nearest the carbon atom to which the hydrogen atom is bound, and repulsion between neighboring hydrogens. The first two components may be considered to remain fairly constant from one vibra-

TABLE 1

Frequencies in benzene and force constants involved in vibrations

FREQUENCY NUMBER	DEGENERACY	BENZENE		BENZENE-d_6		OBSERVED IN
		Calculated	Observed	Calculated	Observed	
1	1	992.6*	992.6	946.6*	946.6	Raman effect
2	1	3061.5*	3061.5	2292.0*	2292.0	Raman effect
6	2	608	606.4	580	581.6	Raman effect
7	2	3107	3048.3	2324	2266.8	Raman effect
8	2	1645	1595	1616	1555.4	Raman effect
9	2	1170	1176.0	863	869.8	Raman effect
10	2	849.7*	849.7	662*	662	Raman effect
11	1	783	670	580	503	Infra-red
18	2	1030	1025	800	813	Infra-red
19	2	1480	1477	1330	1333	Infra-red
20	2	3080	3077	2294	2294	Infra-red

FORCE CONSTANT	VALUE IN 10^5 DYNES PER CM.		FORCE CONSTANT	VALUE IN 10^5 DYNES PER CM.	
	Benzene	Benzene-d_6		Benzene	Benzene-d_6
K (C—C stretching)	7.58	7.62	H (C—H bending in plane)	0.76	0.78
q (C—H stretching)	5.05	5.11	h (C—H bending out of plane)	0.34	0.34
k (C—C—C bending)	0.65	0.65	κ (C—C bond torsion)	0.23	0.23

* These frequencies were used for direct calculation of force constants.

tion form to the next, and thus may be said to determine the "basic value" of H. The remainder of H is composed of hydrogen–hydrogen repulsion, which varies greatly from one vibrational mode to another. In the planar bending frequency ν_3, for example, the hydrogen–hydrogen distance does not change, whereas in ν_9 or ν_{14} the distance alters quite significantly.

The repulsion between the hydrogens bound to adjacent carbon atoms can be calculated fairly well from Morse's equation (15) after the manner of Eyring (7). The Morse expression does not include van der Waals or ionic forces. The latter we neglect, and the contribution of the former is

calculated by the well-known equation of London (13). The net contribution of hydrogen–hydrogen interaction to H for the various modes of vibration is:

Vibration No.	3	9	14	18
Contribution of repulsion, in 10^5 dynes per centimeter	0	0.11	0.17	0.11

It is thus apparent that the effect of repulsion may be considerable. The "basic value" of H, which is to be used to calculate ν_3, is obtained by subtracting 0.11 from the value of H furnished by ν_9 and ν_{18}. H for ν_{14} then results from the addition of 0.17 to the basic value.

Calculated values of the five planar unobservable frequencies are listed in table 2. The "τ-ratio" given by Teller's theorem is tabulated with the τ's obtained from our calculated frequencies. The agreement of the τ's does not assure the correctness of the calculated frequencies, but it does indicate that frequency product ratios are not incorrect.

TABLE 2

Calculated frequency values

FREQUENCY NUMBER	PRESENT PAPER			KOHLRAUSCH		INGOLD		TELLER'S τ	
	Value of H	C_6H_6	C_6D_6	C_6H_6	C_6D_6	C_6H_6	C_6D_6	Theoretical	Calculated
3	0.65	1190	930	1258	1058	1240	940	1.29	1.28
12		1008	960	1000	948	766	730		
13		3063	2294	3056	2296	3062	2294	1.41	1.40
14	0.82	1854	1844	1852	1842	1720	1640		
15	0.82	1145	816	1094	838	1145	820	1.41	1.40

It is readily seen that the three independent calculations are in good agreement. The one real discrepancy in the table is the disagreement on ν_{12}. Ingold and coworkers place this frequency at about 770 cm.$^{-1}$ Their evidence is of a wide variety and in some respects convincing. They estimate the ratio ν_{12}/ν_6 as $\sqrt{8/5}$ on the assumption that the only force constant involved is k. This ratio leads to the calculated value of 766 cm.$^{-1}$ for ν_{12}. To support their value, they offer the extremely faint Raman line found by Grassman and Weiler (8) at 781, and in addition the strong infra-red band at 773. Further evidence appears in the resonance emission spectrum, in which bands indicating a fundamental at 765 appear. The expected shift for deuterium of about 35 cm.$^{-1}$ shows up approximately on the Raman effect, in which the frequency appears at 750; the infra-red maximum, however, changes by only 20 cm.$^{-1}$ In resonance emission, moreover, the deuterium frequency drops to 707, which is 60 cm.$^{-1}$ away from the benzene frequency. These latter benzene-d_6 values thus mitigate somewhat the force of the evidence presented by the benzene spectra.

In opposition to these arguments, it may be offered that it is a rather doubtful procedure to make the simplifying assumptions which are necessary to obtain the ratio $\sqrt{8/5}$ for ν_{12}/ν_6, especially so since ν_6 is the root of a quartic equation. Furthermore if a value of 1000 cm.$^{-1}$ is assumed for ν_{12}, the resultant k is identical with that obtained by solving the quartic equations for k by either of two approximation methods. The experimental evidence submitted by Kohlrausch likewise bears weight: mono-, *m*-di-, and symmetrically tri-substituted benzenes show in the Raman effect a strong, *polarized* line at 1000 cm.$^{-1}$ which has a surprisingly constant value and which is undoubtedly a totally symmetrical vibration. These latter characteristics indicate that the frequency arises from a vibration form such as that for ν_{12}. This frequency appears in benzene-d_1 at 1008 cm.$^{-1}$, which must be quite close to the actual value for benzene. The decision is not an easy one to make, but we feel that the evidence rather favors the assignment $\nu_{12} = 1000$ cm.$^{-1}$

There is one additional discrepancy in table 2, which appears in the values for ν_{14}, but these frequencies are quite high, and an error of 100 cm.$^{-1}$ has very slight effect on the entropy calculations. The evaluation of the planar unobserved frequencies is therefore rather satisfactory for our purposes.

The four out-of-plane distortion frequencies account for six degrees of freedom. These frequencies involve a carbon–carbon bond torsion, resistance to which is measured by the force constant κ. No precedent for the value of κ exists, but if it be assumed that it is of the same order of magnitude as other bending constants, it should lie somewhere in the range 10^4–10^5 dynes per centimeter, and the frequencies involving it should be among the very lowest in benzene. This presumption has led some investigators to attribute the frequency of approximately 160 cm.$^{-1}$, which has appeared in certain electronic spectra, to fundamental vibrations of the out-of-plane type. Several investigators, however, have found a line in the Raman spectrum of benzene at 406 cm.$^{-1}$ The existence of this line cannot be doubted; its interpretation is therefore essential to a complete picture of the vibrational scheme. This interpretation may be one of several alternatives: the line may be a fundamental or some type of combination tone. We will mention presently evidence against the 160 cm.$^{-1}$ fundamental which appears to rule out the possibility that the line is an overtone or combination of lower frequencies. Assignment to a difference tone is reasonable, but no allowed combination of the lower benzene frequencies (606, 670, 850) with higher frequencies will produce 406 cm.$^{-1}$ with the possible exception of $\nu_3 - \nu_{10}$. It seems highly doubtful that a line violating the selection rules should be able to break through the further barriers of the Boltzmann factor and of the low intensity of combination tones in general. Difference tones involving only fundamentals of 1000

cm.$^{-1}$ or higher are unlikely because of the very small value of the Boltzmann factor.

There is also constructive evidence that 406 is a fundamental. It is true that these distortion frequencies should not appear in the Raman effect as fundamentals, but there is a possibility that in the force fields of a liquid, the selection principles are abrogated to some extent. An alternative explanation might be that the line is due to a molecule such as $C^{13}C_5^{12}H_6$ or C_6H_5D, both of which possess the proper symmetry to allow the nonplanar frequencies to appear in the Raman effect. In this connection, it should also be pointed out that the closely related molecule of pyridine, C_5H_5N, which also possesses this symmetry (C_{2v}), exhibits at 404 cm.$^{-1}$ a Raman line of somewhat less than moderate intensity (12). This line in pyridine has an intensity which is rather larger than one would expect from a difference tone.

Further evidence is furnished by a frequency shift of 790 cm.$^{-1}$ found by Cuthbertson and Kistiakowsky (5) and by Ingold and Wilson (9-VI) in the

TABLE 3

Frequencies calculated from Wilson's equations

FREQUENCY NUMBER	DEGENERACY	BENZENE	BENZENE-d_6
4	1	538	395
5	1	1520	1480
16	2	406	314
17	2	1160	1070

resonance emission spectrum of benzene. This shift corresponds to a possible fundamental at 395 cm.$^{-1}$, and as Ingold and Wilson point out (9–VI, p. 966), the fundamental might be attributed to one of the out-of-plane frequencies. Corresponding evidence for benzene-d_6 is lacking.

Ingold and associates (9-III) have reported tentatively a doubtful frequency at 337 cm.$^{-1}$ in the Raman spectrum of benzene-d_6. This line may correspond to the 406 frequency in benzene, although it is conceivable that 337 cm.$^{-1}$ is the difference frequency $\nu_3 - \nu_{10}$.

On the basis of the preceding evidence, the frequency 406 cm.$^{-1}$ in benzene is attributed to one of the two low frequencies ν_{16} or ν_4. Somewhat arbitrarily we make the assignment $\nu_{16} = 406$. ν_{16} should be lower than ν_4, and by making this assignment we have obtained a value for the force constant κ which is reasonably close to those of the other bending constants. The frequencies listed in table 3 are those calculated from Wilson's equations. The value of κ used was 0.23×10^5 dynes per centimeter, and that of h was 0.34×10^5.

STATISTICAL CALCULATIONS

The results given in tables 1, 2, and 3 have been used to calculate a spectroscopic value of S_g. The moments of inertia were determined from the geometry of the molecule, the C–C distance being taken as 1.40 A.U. and the H–H distance as 1.14 (10, 18). The results of the calculations are listed in table 4. In obtaining the entropies in table 4, nuclear spin has been ignored and the contribution of electronic levels in benzene above the non-degenerate ground state has been neglected.

TABLE 4

A. Entropy of benzene vapor at 1 atmosphere from statistical mechanics

ENTROPY OF	BENZENE		BENZENE-d_6	
	298°K.	353.2°K.	298°K.	353.2°K.
Translation	38.98	39.83	39.21	40.05
Vibration	4.75	7.01	7.55	10.50
Rotation	25.72	26.23	26.31	27.07
Symmetry term: $-R \ln \sigma$ ($\sigma = 12$)	−4.93	−4.93	−4.93	−4.93
Total	64.52	68.14	68.14	72.69

Moments of inertia in gram-cm.^{2}: Benzene: $A = 148.6 \times 10^{-40}$; $C = 297.2 \times 10^{-40}$; Benzene-$d_6$: $A = 180.7 \times 10^{-40}$; $C = 361.4 \times 10^{-40}$

B. Thermal entropy of benzene vapor at 1 atmosphere

ENTROPY OF	RANGE	REFERENCE	TEMPERATURE OF VAPOR	
			298°K.	353.2°K.
Solid	0°–90°K.	(1)	10.89 ± 0.2	10.89 ± 0.2
	90°–M.p.	(17)	20.00 ± 0.2	20.00 ± 0.2
Fusion	M.p. = 278.5°K.	(2, 17)	8.43 ± 0.0	8.43 ± 0.0
Liquid	278.5°–298°K.	(17)	2.15 ± 0.0	2.15 ± 0.0
	298°–253.2°K.	(2, 17)		5.83 ± 0.05
Vaporization		I.C.T. and 14	27.36 ± 0.15	20.85 ± 0.05
Compression			−4.16 ± 0.05	
			64.67 ± 0.6E.U	68.15 ± 0.5E.U

The agreement of spectroscopic and thermal entropies indicates definitely a symmetry number of 12, i.e., benzene must have plane hexagonal symmetry. An assumed σ of six would lead to disagreement in the entropies of about 1.4 E. U.

It seems appropriate at this point to consider the validity of the sort of calculation which we have made. In the first place, the method requires thermal data of considerable accuracy. In the present instance, the

thermal data are trust-worthy, probably more so than is indicated by the liberal estimate of error of 0.5 E. U. Even if the error is 0.5 E. U., however, one can still decide between 6 and 12 for the symmetry number. It is presumed that the thermal data are free from such orientation effects in the crystalline state as have been found by Giauque (4) for carbon monoxide and other molecules. These effects make the thermal entropy too low, and hence always lead to a value of σ which is too high. There seems to be no reason to suspect that such effects are actually present in crystalline benzene.

Secondly, the method necessitates a complete vibrational analysis, that is, a knowledge of all frequencies and degeneracies. We can summarize our analysis in this fashion:

(1) The eleven observed frequencies accounting for nineteen degrees of freedom are known accurately enough so that the error in the vibrational entropy due to uncertainty in these frequencies is less than 0.5 E. U. at 298°K.

(2) The five planar unobserved frequencies all lie above 1000 cm.$^{-1}$, with the possible exception of ν_{12}. Hence the error in the entropy because of inaccurate knowledge of these vibrations is hardly more than 0.05 E. U. If ν_{12} has a value in the region around 770 cm.$^{-1}$, the error rises to 0.2 E. U. at the most.

(3) Because the preceding sources of error are small, it is seen that the entire analysis rests on the assignment of ν_{16} to the 406 frequency. If the assignment is correct, the calculated value of ν_4 is probably not far wrong. The other torsional frequencies are quite high, and while they may be considerably in error, their contribution to the entropy is slight. Assuming the assignment is correct, the error in the entropy due to the out-of-plane frequencies may be roughly set at 0.4 E. U., bringing the total possible error to 0.5–0.6 E. U.

If ν_{16} does not have the value of 406 in benzene, we are faced with a number of alternatives:

(1) ν_{16} may be *higher* than 406. The vibrational entropy then lies somewhere between the listed value and about 2 E. U. lower. This possibility would indicate a minimum symmetry number of about six.

(2) If ν_4 instead of ν_{16} has the frequency 406 the vibrational entropy is *increased* by an entropy unit or so, and the disagreement with experimental values becomes marked. In this eventuality, a symmetry number of twelve is definitely indicated, with the additional discrepancy between theory and experiment perhaps to be attributed to trouble in the crystalline state.

(3) If it be assumed that ν_4 or ν_{16} is to be identified with the 160 cm.$^{-1}$ frequency found in electronic spectra, then unless the theory is completely meaningless, there must be *three* degrees of freedom 200 cm.$^{-1}$

or lower. These would make an entropy contribution of some 5 E. U. and cause a discrepancy with experiment of more than 3 E. U. at 298°K. For this reason the possibility of a fundamental frequency in benzene as low as 160 cm.$^{-1}$ seems definitely ruled out.

In conclusion it may be recalled that a symmetry number of twelve is compatible with the best evidence of x-ray and electron-diffraction studies on benzene. The theories of the electronic structure of the benzene ring likewise predict planarity. It may further be remarked that hydrogen–hydrogen repulsion can be shown to be too weak to warp the C—H bond out of the ring plane if the bending constant h calculated from ν_{10} or ν_{11} be made the basis of the calculation. The evidence we have presented is in agreement with all these structural arguments, and, while it is not entirely conclusive, it strongly indicates a plane structure of symmetry D_{6h}.

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BIOGRAPHY

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